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Title of the Invention: Prestressable Layer System for Partition Glass

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(54) Title: PRESTRESSABLE LAYER SYSTEM FOR PARTITION GLASS

(57) Abstract: The inventive prestressable and flexural layer system with a low emissivity is used for a partition glass and is provided with a functional silver layer and a metallic sacrificed layer which is made of Ti or a Ti alloy and of Zn and/or Al and arranged thereunder. Said system also comprises anti-reflection dielectric layers and an oxidised covering layer which is nitrided or oxynitrided. The metallic sacrificed layer contains chemically bound hydrogen. A ZnO layer eventually stimulated with Al and/or In is adjacent to the metallic sacrified layer. The covering layer comprises a titanium compound. The analogous layer systems can be produced in a comparatively economical manner exhibiting a high hardness and chemical resistance. The colour parameters of said systems are easily reproducible even when they are thermally treated at a high temperature.

Prestressable Layer System for Partition Glass

The invention relates to a system of layers with low emissivity, capable of being highly heat stressed, for partition glass, with silver as a functional layer, a sacrificed metal layer, antireflective dielectric layers and an oxidized, nitrided or oxynitrided cover layer arranged above the silver layer.

Layer systems with low emissivity must be capable of being highly heat stressed when the coated partition glass is subjected to a bending and/or prestressing operation. Although heat-stable layers are not necessary when the partition glass is only coated after bending and prestressing, this presents the disadvantage that it is not always possible to avoid coating defects[1]. These defects result from the fact that the heat treatment operation often causes local modifications on the glass surface that become visible after coating. In particular, coating that precedes heat treatment also enjoys the economic advantage of simplifying the coating operation, since large partition glass structures in large industrial installations can be coated. The desired formats are then cut in the large coated glass and curved and/or prestressed in the customary manner.

Layer systems capable of being highly heat stressed are known in different embodiments. In a first group of layer systems capable of being highly heat stressed, the anti-reflecting layers each consist of Si_3N_4 and are separated from the functional silver layer by thin sacrificed metal layers of CrNi. Layer systems having this structure are described, for example, in the documents EP 0 567 735 B1, EP 0 717 014 B1, EP 0 771 766 B1, EP 0 646 551 B1 and EP 0 796 825 A2.

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[1] **Translator's Note**: the French source text might be a bit unclear at this point in that it juxtaposed something that is "not necessary" and then proclaims "this presents the disadvantage…." We believe that this grammatical juxtaposition may obscure the intended meaning, as we understand it, namely that regardless of whether one can avoid having to deal with heat-stable layers by coating only AFTER bending or pre-stressing, that certain disadvantages STILL exist, namely the problem of coating defects when coating bent or prestressed partition glass and overall, that coating prior to bending and prestressing is just simpler and more economical, which is why one should not have to avoid heat-stable layer systems. Since we cannot consult the authors, this simply represents our interpretation of the intended meaning, but the translation as is, represents a correct reflection of the French.

The layer system described in EP 0 883 585 B1 also belongs to this group, but, in this case, the sacrificed metal layer consists of Si. Although such layer systems are very heat-stable, they are very costly to produce, because of the known problems posed during sputtering of nitrides. In addition, spraying of relatively thick Si_3N_4 layers remains problematical, because of the mechanical stresses in the layers.

A second group of layer systems capable of being highly heat stressed includes those, which, in addition to nitrided layers, like Si_3N_4 of AlN, also have oxidized layers, especially in the zone of the covering layer. DE 196 40 800 C2, for example, describes a layer system, in which an intermediate metal nitride or oxynitride layer of the sacrificed metal layer is arranged between the blocking metal layer and the oxidized or nitrided covering layer. Another layer system of this type, known from DE 101 05 199 C1, is characterized by the fact that an Si_3N_4 or AlN layer is arranged between the silver layer and the sacrificed metal layer. In the layer system known from EP 0 834 483 B1, an intermediate TiO_2 layer with a thickness of at least 5 nm is arranged between a sacrificed Ti metal layer and the covering layer, and an oxide, nitride or oxynitride covering layer of Bi, Sn, Zn or a mixture of these metals is arranged on this intermediate layer. Both the intermediate Si_3N_4 or AlN intermediate layers and the thick TiO_2 layers are complicated to produce. In addition, thick layers with a high refractive index made of TiO_2 impose increased requirements on the regularity of the layer thickness and, beyond slight deviations in thickness of the layer, can cause color errors after the prestressing operation.

In a third group of layer systems capable of being highly heat stressed, the individual layers consist of purely oxidized layers, except for the functional layer and the sacrificed metal layer. Since oxidized layers can be sputtered most of the time without problem, such layer systems are economical to produce. However, the sacrificed metal layer in this case has a relatively high thickness. A system of layers of this type is described, for example, in DE 198 52 358 C1. The sacrificed metal, in this case, consists of an aluminum alloy with one or more of the elements Mg, Mn, Cu, Zn and Si as alloy components.

A purely oxidized layer system for partition glass that must be suitable for a bending and/or prestressing operation is described in EP 0 233 003 B1. In this known layer system a layer of Al,

Ti, Zn or Ta with a thickness from 4 to 15 nm is arranged above the silver layer. Preferably, a layer of Al, Ti, Zn or Ta is also arranged below the silver layer.

An oxidized layer system that must be suitable for bending and/or prestressing is described in DE 39 41 027 C2. In this known layer system a layer of ZnO with a thickness of at most 15 nm is arranged below the silver layer and the covering of the silver layer is a sacrificed metal oxide of the titanium, aluminum, stainless steel, bismuth, zinc group or mixtures of these oxides, which is formed by means of the deposition of the sacrificed metal and its conversion to oxide.

The reflection tint of all the known layer systems is modified more or less visibly after the necessary heat treatment for the bending and/or prestressing of the partition glass. Generally, the glass also has increased emissivity after the heat treatment and an increased proportion of light diffusion. Because of modification of the reflection tint, one recognizes with the naked eye partition glass that has been coated and heat treated and incorporated in the same façade next to partition glass that has not been heat treated, but has the same system of layers. For this purpose, a different layer system is therefore necessary, one capable of being prestressed and whose properties are comparable to those of a non-heat-treated layer system.

Simultaneous observance of three important conditions, namely, maintenance of a narrowly defined reflection tint and, if possible, no increase, or only a slight increase in the amount of diffused light and emissivity by the heat treatment operation, is increasingly more difficult to achieve when the requirements are increased in terms of the neutrality of the tint of the layer system.

The problem underlying the invention therefore consists of developing a layer system of neutral tint with essentially oxidized anti-reflecting layers, which, after a heat treatment operation, necessary, for example, for curvature and/or prestressing of the partition glass, have essentially the same tint parameters in reflection as a predetermined oxidized layer system that is not heat treated, and in which heat treatment increases the amount of diffused light and emissivity as little as possible. At the same time, the layer system must present increased hardness and high chemical resistance.

According to the invention, this problem is solved in that the sacrificed metal layer consists of Ti or an alloy of Ti and Zn and/or Al, and contains chemically bonded hydrogen, and a layer of ZnO, optionally doped with Al and/or In, is connected to the sacrificed metal layer, and that the covering layer consists of a titanium compound.

Layer systems having the structure according to the invention can be produced relatively economically and have an increased hardness and high chemical resistance. However, they are characterized, in particular, by the fact that their color appearance can be modified in a controlled fashion and reproducibly with a heat treatment operation even a high temperature, and that they only exhibit a very slight increase in the amount of diffused light and low emissivity.

The composition of the sacrificed metal layer that is sputtered in a gas working atmosphere of Ar/H_2 plays a particular role. Since metallic Ti has the property of bonding to hydrogen, the effect of protecting the sacrificed metal with respect to the silver layer is further reinforced by a reducing "hydrogen buffer". Hydrogen of the sacrificed metal layer can be detected with the help of appropriate analytical methods.

Titanium alloys containing 50 to 80 % by weight of Ti and 20 to 50 % by weight of Al have proven suitable, in particular, for the sacrificed metal layer.

Arrangement of the ZnO layer, optionally doped with Al or In, directly on the sacrificed metal layer makes a considerable contribution to the desired result. This ZnO layer can have a thickness so that it itself already represents the anti-reflecting layer, so that the covering layer immediately follows this ZnO layer. However, it is also possible to provide only a relatively thin ZnO layer that then acts as a partial layer of the anti-reflecting layer, whereas the partial layer of the anti-reflecting layer that is connected to it consists of SnO_2, for example. But in this case it is necessary that the thickness of the ZnO layer reach at least 3 nm.

The covering layer of the layer system is preferably a mixed oxide with a spinel structure, but binary alloys of the Ti/Al type are also suitable. The following compounds are particularly

suitable for the covering layer: $ZnO:Al/TiO_2$, $ZnO:Al/Ti$, $Zn_xSn_yO_z/TiO_2$, $Zn_xSn_yO_z/Ti$, $Zn_xTi_yAl_zO_r$, $Ti_xAl_yO_z$, Ti_xAl_y, $Ti_xAl_yN_z$, $Ti_xAl_yO_zN_r$, $Zn_xSn_ySb_zO_r/TiO_2$, $Zn_xSn_ySb_zO_r/Ti$ or $Zn_xSn_ySb_zO_r/TiO_2$. Since titanium alloys are involved here, they represent the condition of the covering layer before the heat treatment operation, during which they are then converted to the oxidized form.

Preferred compositions of the sacrificed metal layer and other layers of the layer system, as well as the preferred thickness ranges of the individual layers, will follow from the dependent claims.

The invention is described in greater detail below by means of a practical example, which is compared to a comparative example of the prior art. In order to evaluate the properties of the layers, the measurements and tests mentioned below are conducted on the coated partition glass.

A. Measurement of transmission T at 550 nm of a coated partition glass

B. Measurement of the reflection tint parameters in a laboratory system (DIN 5033), using an ISO zero standard as tint reference. Fixed tolerance values Δ, which are defined as follows for the layer system at issue here in the prestressed state, must be maintained in the tint parameters of this reference standard: $\Delta L = \pm 3.0$; $\Delta a = \pm 1.4$; $\Delta b = -3.5$ to $+1.0$.

C. Measurement of the surface electrical resistance with a FPP 5000 Veeco instrument and the manual measurement apparatus SQO HM-1.

D. Measurement of emissivity E with the Sten Löfving MK2 apparatus.

E. Sweating test with water according to DIN 50017 with visual evaluation.

F. Measurement of electrochemical resistance (EMK test); this test is described in Z. Silikattechnik 32 (1981), page 216. The test permits a conclusion concerning the quality of passivation of the covering layer situated above the silver layer, as well as the corrosion behavior of the Ag layer.

G. Erichsen washing test according to ASTM 2486, visual evaluation.

H. Measurement of scratch hardness; a needle, loaded by a weight, is pulled along the layer at a defined speed. The weight, in g, for which traces of scratches are visible, serves as a measurement of the scratch hardness.

I. Measurement of diffused light, in %, with a diffused light measurement apparatus from the Gardner company.

Comparative example

The following layer system is applied on a continuous industrial coating installation from the prior art (DE 39 41 027) with a reactive cathode sputtering process, maintained by a magnetic field on the float glass, the thickness of the individual layers being given each time in nm:

glass/3TiO_2/22SnO_2/13ZnO:Al/ 12Ag/5TiAl/20SnO_2/10TiO_2

The ZnO:Al layer is sputtered under reactive conditions from a metal ZnAl target with 2 % by weight of Al. The sacrificed metal layer is sputtered from a metal target containing 64 % by weight of Ti and 36 % by weight of Al. The covering layer is arranged as a result of reactive sputtering from a metallic titanium target.

Performance of the above tests on several samples before heat treatment yields the following average values:

A. Transmission	T_{550} = 76 – 77%
B. Tint parameters	ΔL – 0.1 Δa 4.47 Δb – 5.31
C. Surface resistance	R = 6.8 – 6.9 Ω
D. Emissivity	E = 7.8
E. Water sweating test	Red spots
F. EMK test	140 mV
G. Washing test	Beginning of detachment of the layer after 350 passes
H. Scratch hardness	60 – 210 g
I. Diffused light	0.17%

Several different coated samples, measuring 60 × 80 cm, are heated to 680 – 700°C and prestressed by means of abrupt cooling. The tests and the measurements described later are then carried out on the prestressed glass. The water sweating test, the EMK test, the washing test and the scratch hardness test are not performed, because, by experience, it is known that these values do not deteriorate after the heat treatment operation. The performed tests yield the following results:

A. Transmission	T_{550} = 88.%
B. Tint parameters	ΔL 1.3 Δa 1.56 Δb – 3.95
C. Surface resistance	R = 4.0 – 4.6 Ω
D. Emissivity	E = 5.8 – 6.8%
I. Diffused light	0.35%

The increase, as a result of the heat treatment, in the amount of diffused light from 0.17% to 0.35% is still tolerable. However, an emissivity of 5.8 – 6.8% is too high to produce insulating partition glass having a k value of 1.1 W/m^2K. The tint parameters, after prestressing, are

beyond the tolerance limits. The partition glass in reflection has a bluish-red appearance. Broad variations in thickness of the different layers no longer permit a reflection tint of neutral color to be obtained with the sought tint values.

Practical example

In the same coating installation as in the comparative example the following layer system according to the invention is produced, using a metal target consisting of an alloy of 64 % by weight of Ti and 36 % by weight of Al, both for deposition of the sacrificed metal layer and for deposition of the covering layer:

glass/25SnO_2/9ZnO:Al/11.5Ag/2TiAl(TiH_z)/5ZnO:Al/33SnO_2/3$Ti_xAl_yO_zN_r$

Deposition of the sacrificed metal layer is carried out in a mixture of working gas Ar/H_2 (90/10 vol%) and deposition of the oxynitrided covering layer in a working gas mixture of Ar/N_2/O_2.

The measurements and tests on the coated partition glass, before heat treatment, yield the following values:

A. Transmission	T_{550} = 78.3%
B. Tint parameters	ΔL – 0.9 Δa 2.80 Δb – 3.8
C. Surface resistance	R = 5.7 Ω
D. Emissivity	E = 6.6 – 6.7%
E. Water sweating test	No defect
F. EMK test	-64 mV
G. Washing test	No attack after 1000 passes
H. Scratch hardness	150 – 260 g
I. Diffused light	0.18%

After prestressing, the same measurements and tests are carried out on several samples as for the prestressed partition glass of the comparative example. The tests yield the following results:

A. Transmission	$T_{550} = 88.3\%$
B. Tint parameters	ΔL 1.0 Δa 1.2 Δb – 2.4
C. Surface resistance	R = 3.6 – 4.0 Ω
D. Emissivity	E = 4.8 – 5.0%
I. Diffused light	0.27%

The obtained values reveal distinct improvements, both in the layer not heat treated and in the heat-treated layer. In particular, the heat-treated layer satisfies the predetermined tint parameters. The reflection tint is distinctly more neutral than in the comparative example. The functional dependence between surface resistance and emissivity better corresponds to the physical dependence and permits production of insulating partition glass with a K-value of 1.1 W/m^2K. The amount of diffused light is increased distinctly less in response to the heat treatment than in the case of the comparative example. This indicates that the Ag layer is only slightly destructured. The result of the other tests, for example, the water sweating test, the EMK, the washing test and the scratch hardness test, which were carried out on the non-heat-treated samples, are better, on average. The layer system can be produced in stable and reproducible fashion in an industrial coating installation.

CLAIMS

1. A layer system with low emissivity, capable of being highly heat stressed, for partition glass, with silver as a functional layer, a sacrificed metal layer arranged above the silver layer, anti-reflecting dielectric layers and an oxidized, nitrided or oxynitrided covering layer, characterized by the fact that the sacrificed metal layer consists of Ti or an alloy of Ti and Zn and/or Al and contains chemically bonded hydrogen, and that a ZnO layer, optionally doped with Al and/or In, is connected to the sacrificed metal layer, and that the covering layer consists of a titanium compound.

2. The layer system according to Claim 1, characterized by the fact that the sacrificed metal layer consists of a TiAl alloy containing 20 to 50 % by weight of Al.

3. The layer system according to Claim 1 or 2, characterized by the fact that the sacrificed metal layer has a layer thickness of 1 to 5 nm.

4. The layer system according to Claims 1 to 3, characterized by the fact that the ZnO layer contains 0.5 to 10 % by weight of Al and/or In.

5. The layer system according to Claim 4, characterized by the fact that the ZnO layer has a thickness of at least 3 nm.

6. The layer system according to one of the Claims 1 to 5, characterized by the fact that a layer of SnO_2, Si_3N_4, ZnO, Al_2O_3 and/or SiO_2 is arranged as a partial layer of the anti-reflecting upper dielectric layer between the ZnO layer and the covering layer.

7. The layer system according to one of the Claims 1 to 6, characterized by the fact that the covering layer consist of ZnO:Al/TiO_2, ZnO:Al/Ti, $Zn_xSn_yO_z/TiO_2$, $Zn_xSn_yO_z$/Ti, $Zn_xTi_yAl_zO_r$, $Ti_xAl_yO_z$, Ti_xAl_y, $Ti_xAl_yN_z$, $Ti_xAl_yO_zN_r$, $Zn_xSn_ySb_zO_r/TiO_2$, $Zn_xSn_ySb_zO_r$/Ti or $Zn_xSn_ySb_zO_r/TiO_2$.

8. The layer system according to one of the Claims 1 to 7, characterized by a layer structure glass-SnO_2-ZnO:Al-Ag-TiAl(TiH_x)-ZnOAl-$SnO_2Ti_xAl_yO_zN_r$.